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IGM88AP-101-745-G
CNRC 29097

Room-Temperature Aging of Narmco 5208 Carbon-Epoxy Prepreg
Part I. Physicochemical Characterization

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ABSTRACT

Samples of Narmco Rigidite 5208/WC3000 carbon-epoxy prepreg were exposed to ambient temperature (22°C) and 50% relative humidity for different periods of time up to 66 days. They were analyzed in depth using various techniques to determine the extent of the chemical changes occurring. The physicochemical techniques used were Fourier transform infrared spectroscopy (transmission, attenuated total reflection, diffuse reflection), liquid chromatography (reverse-phase, high-speed reverse-phase, and high-performance size-exclusion), thermal analysis (differential scanning calorimetry and thermogravimetric analysis), and pyrolysis – gas chromatography. All showed evidence of significant changes, the most sensitive being Fourier transform infrared spectroscopy (FT-IR) and reverse-phase liquid chromatography (RPLC). FT-IR showed that the number of unreacted epoxy groups decreases steadily at a rate of 0.34% per day, based on the initial amount. At the same time, the number of free amine-hardener molecules, as monitored by RPLC, drops at a rate of 1.05% per day. RPLC also showed that the amount of initial epoxy-amine reaction product increases significantly over the first thirty days but then declines as it undergoes further reaction to give higher-molecular-weight products. The heat of polymerization of the resin, measured by thermal analysis, decreased by 0.26% per day from its initial value of 561 J/g.

INTRODUCTION

Physicochemical characterization of high-performance composite materials consisting of high-strength reinforcing fibers embedded in an organic polymer matrix is becoming more common in quality control laboratories. Specific analytical methods such as infrared spectroscopy (1,2), liquid chromatography (3-5), thermal analysis (6), and pyrolysis – gas chromatography (7) have been developed for characterizing carbon-epoxy prepregs. Since these materials contain a reactive mixture of epoxy resin and hardener, chemical reactions can occur which will change the physical properties and can affect the long term mechanical performance of parts made from the prepreg.

The work described herein involves a comprehensive study of one particular prepreg system (Narmco Rigidite 5208/WC3000) when exposed to room temperature and 50% relative humidity over a period of 66 days. The aims of the work were to determine the magnitude of the changes in terms of chemical composition and to compare the sensitivity of the different analytical methods for detecting these changes.

There are few published data concerning the aging of Narmco 5208. Crabtree (8) has shown that the ratio of certain peaks in size-exclusion chromatography varies linearly with aging time when the resin is exposed at ambient temperature. Hinrichs and Thuen (9) studied Narmco 5208 using high-performance liquid chromatography (HPLC), moisture analysis, and rheological measurements. When prepreg is exposed to 50% or higher relative humidity, the moisture reaches a saturation level of about 0.7% in 5 hours. HPLC could detect no changes in prepreg exposed for 5 days at room temperature and 0% or 98% R.H. A high moisture content was found to increase the tackiness, to affect the viscosity profile during cure, and to produce porosity in the laminate. Lawless (10) used dynamic dielectric analysis (DDA) to study the aging of Narmco 5208 in prepreg exposed at room temperature in both dry (0% R.H.) and wet (100% R.H.) conditions. In both cases, the prepreg became noticeably more rigid after 2-3 weeks. The DDA curves showed changes even after one day.

This paper gives the physicochemical results obtained in a more complete study of the Narmco 5208 system. In a subsequent paper (11), the results obtained by physical and mechanical testing will be described and compared with the physicochemical data.

EXPERIMENTAL SECTION

Materials

The composite system studied was Rigidite 5208/WC3000-42", sold by BASF Structural Materials Inc., Narmco Division (Anaheim, CA). The reinforcement consists of Celion graphite fibers, 3000 fibers per yarn, woven in an 8-harness satin pattern. The woven fabric is impregnated with Narmco 5208 resin to a nominal resin content of 42% by weight and the prepreg is supplied on a plastic backing sheet in rolls 42 inches wide. The recommended cure schedule consists of a one-hour dwell at 275°F (135°C) followed by a two-hour cure at 350°F (177°C). It has been reported (12-16) that Narmco 5208 consists primarily of three components. The major epoxy, which accounts for about 70% by weight, is based on TGDDM (tetraglycidyldiaminodiphenylmethane). The second most important component (about 22% by weight) is the curing agent DDS (diaminodiphenylsulfone). There is also a minor epoxy (about 8% by weight) which is of the bisphenol A Novolac type. The chemical structures of these components are given in Fig. 1. The DDS is a relatively pure material, but the epoxy resins consist of a mixture of monomer, oligomers, and other products (starting materials and by-products).

Exposure conditions

The prepreg (Batch Number 1014), which was stored in a freezer until used, was thawed, unrolled, and cut into twenty-three sheets approximately eight feet long. Of these, twenty were hung lengthwise in a rack in a controlled-atmosphere laboratory. The plastic backing sheet was left in place, so that only one side of the prepreg was fully exposed. Temperature and relative

humidity were monitored frequently over the 66-day exposure period. The average values were 21.5 ± 0.7 °C for the temperature and 49.2 ± 2.4 % for humidity. Of the remaining three sheets, one was the "control" sample, one was stored in a freezer at -25°C and one was sealed in a plastic bag with "Drierite" desiccant and kept in the same laboratory as the suspended sheets. At chosen intervals over a period of 66 days, one sheet of prepreg was removed from the rack for characterization. The sheet stored under dry conditions was tested after 50 days, and the sheet stored in a freezer after 87 days.

Chemical testing procedures

All the analytical methods used have already been described in detail elsewhere and hence will not be repeated here. They include Fourier transform infrared spectroscopy (transmission, attenuated total reflection, diffuse reflection) (1,2), reverse-phase liquid chromatography (3), high-speed reverse-phase liquid chromatography (4), high-performance size-exclusion chromatography (5), differential scanning calorimetry and thermogravimetry (6), and pyrolysis – gas chromatography (7).

RESULTS AND DISCUSSION

Infrared spectroscopy

Transmission

A typical Narmco 5208 transmission spectrum is shown in Fig. 2. The peaks used for quantitative analysis are the aromatic ring band at 1517 cm^{-1}, the epoxide ring bands at 973, 952, and 906 cm^{-1}, and the DDS (sulfone) bands at 1146, 1105, and 1073 cm^{-1}. Dividing the epoxide band area by the aromatic ring band area gives an "epoxide index" which is a measure of the number of unreacted epoxide groups in the resin and is thus related to the degree of aging. Similarly, taking the ratio of the sulfone band against the aromatic band gives a "sulfone index"

which is a measure of the total amount of DDS hardener in the system. Since the sulfone groups are not destroyed in the curing reaction, this index should not be significantly affected by aging. For both epoxide and sulfone a "single" or a "multiple" index can be calculated depending on whether one or several peaks are used in the calculation. Thus the "single sulfone" index is based on only the peak at 1146 cm^{-1}, whereas the "multiple sulfone" index includes the peaks at 1105 and 1073 cm^{-1}. Similarly, the "single epoxide" index is based on the peak at 906 cm^{-1}, while the "multiple epoxide" index involves all three. It should be noted that the presence of three epoxide peaks is characteristic of TGDDM. For many epoxy resins, only the 906 cm^{-1} peak is significant.

The measured indices are shown graphically in Figs. 3 and 4. In these and in subsequent graphs, the error bars correspond to the calculated standard deviations. Both the epoxide indices show a definite decrease with aging time. The variation appears to be linear up to about 50 days, beyond which point some deviation occurs. This may be due to a slowing of the epoxy reaction, but more likely it is related to the fact that the more highly aged samples were not completely soluble in acetone. Linear regression (Table 1) for the points corresponding to less than 50 days shows that both epoxide indices decrease at a rate of 0.34% per day with respect to their initial values. Thus over a period of 50 days the number of unreacted epoxide groups drops by 17%.

Ideally, the sulfone indices should not change, since the sulfone groups are not destroyed by the curing reaction. However, as seen in Fig. 4, they do vary with aging time, especially the single sulfone index, which decreases by about 0.2% per day. The reason for this is not clear, but it has been pointed out that the sulfone bands are affected by the transformation from primary to secondary amine upon reaction with epoxy (17,18), as well as by the presence of moisture (19). The aromatic band could also be sensitive to such effects. Since the multiple sulfone index appears to be less affected than the single sulfone index, it appears to be a better indicator of the total amount of hardener present.

Attenuated total reflection

For this work, only selected samples from the aging study were run, corresponding to exposure times of 0, 14, 42, and 66 days. The object was not to obtain a complete set of data as in the transmission experiment, but rather to compare the two methods. Fig. 5 shows the spectra recorded with a germanium prism for the fresh prepreg and the sample aged for 66 days. There are obvious changes in the shape of the N-H bands (3600-3100 cm^{-1}), the C-H bands (3100-2800 cm^{-1}), and the band near 1600 cm^{-1}, as well as an increase in the intensity of the peak at 1320 cm^{-1}. Also noticeable in the spectrum of the fresh prepreg is the small peak near 1710 cm^{-1}, which is absent from the spectrum of the aged prepreg. This was shown to be due to residual acetone from the impregnation process.

The results obtained for the multiple and single epoxide indices show a linear decrease with exposure time. Linear regression (Table 1) gives slopes corresponding to decreases of 0.36% and 0.32% per day respectively. These are very close to the value of 0.34% obtained by transmission. The sulfone indices also vary somewhat, as observed in transmission. It should be noted that the actual values of the indices obtained are different in transmission and in ATR because of a wavelength dependence in the latter case (2).

It has been demonstrated (2) that in order to obtain reliable results by the transmission method, very careful sample preparation is required in order to produce films with uniform thickness. Attenuated total reflection with a germanium prism is probably the best IR method overall for characterizing Narmco 5208 carbon-epoxy prepreg. Although the precision is slightly poorer than in a carefully performed transmission experiment, it has the important advantage of not requiring solvent extraction of the prepreg and preparation of thin cast films. This saves time and avoids the problem of nonuniform film thickness. The prepreg can be measured as is, even if it has polymerized beyond the point where it is soluble in acetone. In addition, as mentioned above, the presence of acetone in the prepreg can be detected.

Diffuse reflection FT-IR was also used to record spectra of the aged prepreg. However, the quantitative results obtained showed large standard deviations in comparison to the changes observed. Hence, this method is of little use for monitoring the prepreg aging (1,2).

Liquid chromatography

Reverse-phase liquid chromatography

A typical chromatogram is shown in Fig. 6. Nine different peaks were treated quantitatively (peaks 1, 7, 8, 9, 10, 11, 14, 15, 16) and the results were expressed in terms of the normalized peak area with respect to acetophenone internal standard, as well as in terms of the ratio with respect to the TGDDM peak (3). For each sample, two separate specimens were extracted, and for each extraction, three injections were performed. To give a general idea of the results obtained, selected data are given in Table 2. Results are given for the four most important peaks of the chromatogram: DDS (peak 1), TGDDM-DDS reaction product (peak 7), TGDDM (peak 9), and DGEBA (peak 10). The various peaks analyzed will be discussed individually.

Peak 1 corresponds to unreacted amine hardener diaminodiphenylsulfone. Both the actual amount of free DDS and the ratio of DDS to TGDDM show a linear decrease with exposure time, the first by 1.05% per day and the second by 0.85% per day (Table 1). The ratio decreases at a lower rate because the amount of TGDDM decreases concurrently with the DDS. The degree of scatter is considerably less when the peak area is used rather than the peak height (3). This is because this particular peak sometimes shows resolved structure, depending on RPLC column conditions, and when this happens the measured height is affected more than the area. Hence, it is preferable to use area for the calculation.

Peak 7 corresponds to the product of reaction of one molecule of TGDDM with one molecule of DDS. The variation is shown in Fig. 7. Initially the amount increases, but after about 30 days it reaches a plateau and subsequently begins to decrease, as the product undergoes further reaction

with TGDDM or DDS to produce molecules of higher molecular weight. The ratio RP/TGDDM increases up to about 30 days and then remains steady as both RP and TGDDM decrease together.

The compound responsible for peak 8 has not been identified, but it has been established that it arises from the major epoxy. It is included in the analysis because it is one of the stronger peaks in the chromatogram. It shows no significant change over the course of the aging experiment.

The TGDDM peak (peak 9) is the strongest in the chromatogram. It gradually decreases with exposure time. The degree of scatter is about the same whether area or height is used, and appears to be somewhat higher than for the DDS peak. Linear regression gives a slope corresponding to a decrease in TGDDM monomer of 0.38% per day, based on the initial value.

Peak 10 is due to DGEBA, or diglycidyl ether of bisphenol A, the main component of the minor epoxy resin (based on bisphenol A Novolac). Like DDS and TGDDM, it shows a linear decrease with exposure time. The normalized area decreases at a rate of 0.87% per day. This is more than twice the rate for TGDDM, so as a result the ratio DGEBA/TGDDM also decreases with time.

Peak 11 corresponds to a higher-molecular-weight component of the TGDDM-based resin. It too decreases with time, at a rate of 0.96% per day. Unlike peak 8, which also comes from the major epoxy, peak 11 changes with aging time, so it appears to be related to a reactive component of the system and not to an inert impurity or by-product.

Peaks 14, 15, and 16 are probably due to high-molecular-weight oligomers of the Novolac resin. All three decrease with time. Linear regression gives rates of decrease of 0.72%, 0.87% and 1.00% per day, respectively. Most of the distinct peaks in the RPLC chromatogram show a linear decrease with respect to the prepreg exposure time. The main exception is peak 7, the reaction product peak, which increases up to about 30 days and then decreases.

The peak which is the most sensitive to the prepreg aging is peak 1, the DDS peak, which decreases at a rate of about 1% per day. However, a low value for this peak is not necessarily indicative of resin advancement, since it could be due to a low content of DDS in the initial formulation. It can only be used to check resin advancement if it is used in conjunction with other

data. For instance, if a value has been determined for the same batch immediately after it was produced, comparison of the two will indicate whether reaction has occurred. Likewise, if the total content of DDS is known to be normal from infrared analysis (sulfone index), then an unusually low content of free DDS (RPLC peak 1) indicates that resin advancement has occurred. A better "absolute" indicator of the degree of advancement is the reaction product peak, since there is none of this compound in the starting materials. However, the relative error associated with the measurement of this peak appears to be higher than for the DDS peak.

It is interesting to note that the rate of decrease is considerably lower for TGDDM than for DGEBA. If both molecules were equally reactive, one would expect the TGDDM to disappear at the same rate as the DGEBA, or even faster, because it has more epoxy groups per molecule. The results indicate that this is not the case, and that DGEBA appears to be more reactive than TGDDM with respect to DDS hardener.

The results observed here may be compared in a general way with those found for similar systems in the past. For example, in his study of an unspecified TGDDM/DDS formulation aged at ambient temperature, May (20) found that over a 63-day period the content of DDS and TGDDM monomers dropped by 26% and 14% respectively. The corresponding figures in the present study are 66% and 24% for the same period. For Hercules 3501, after 40 days under dry conditions at ambient temperature, Sewell (21) found a drop in free DDS of 35%, compared with 42% in this work. Also with Hercules 3501, Hagnauer (22) found significant changes on aging at 22°C, especially during the first week, when the DDS and TGDDM dropped by 30% and 20% from their initial values. In the present study, a more gradual (linear) decrease was observed, with drops of only 7.4% and 2.7% respectively after one week. The discrepancies between the present results and earlier ones cited may be explained in terms of variations in composition (minor epoxies, catalysts) and exposure conditions. Hinrichs and Thuen (9) have reported some results for the same system used here, Narmco 5208, but the duration of the experiment was only five days (75°F, 0% and 98% R.H.). They detected no significant changes over this period, probably because such changes were smaller than the error of measurement involved. The present study

has shown that small changes do indeed occur, and can be detected if sufficiently sensitive methods are used.

High-speed reverse-phase liquid chromatography

By using columns packed with particles of diameter 3 μm rather than 5 μm or 10 μm, the time required for an RPLC analysis can be substantially reduced (4). Five samples from the aging study were analyzed by this method. The results were calculated in the same way as in RPLC. They are summarized in Table 3. In the following discussion of the different peaks, the abbreviation RPLC refers to the use of a column 30 cm long packed with 5 μm particles, whereas HS-RPLC refers to a column 5 cm long packed with 3 μm particles.

The variation of the DDS peak is similar to that observed in RPLC. Linear regression (Table 1) gives a rate of decrease for the normalized peak area of 1.09% per day, which compares very well with the value of 1.05% obtained with ordinary RPLC. The behaviour of the reaction product peak is also much the same as that observed in RPLC, with a maximum occurring around 30 days. The RP/TGDDM ratio reaches a plateau at the same time.

As in RPLC, the TGDDM monomer peak is the strongest in the chromatogram, and it varies in a similar manner. The rate of decrease (Table 1) is 0.47% per day, compared to 0.38% in RPLC. The discrepancy may be due to the difference in peak resolution between the two methods. The measured peak area may involve contributions from other (minor) peaks which may not be the same in both cases.

The DGEBA peak also shows a linear decrease with exposure time which is similar to that observed in RPLC. The rate of decrease in this case is 0.60% per day, compared to 0.87% per day in RPLC. Although the figures obtained in HS-RPLC are slightly different from those obtained in RPLC, they still show that the DGEBA disappears faster than the TGDDM. As in the previous case, the difference between the two methods may be due to the difference in resolution.

The HS-RPLC results show that this technique can provide the same information as ordinary RPLC, but with significant savings in time and materials. The most useful parameters are the peaks of the hardener DDS (peak 1) and the TGDDM-DDS reaction product (peak 3). As in RPLC, the DDS peak is probably the best choice for monitoring the prepreg aging.

High-performance size-exclusion chromatography

A typical high-performance size-exclusion chromatogram is given in Fig. 8. The solutions analyzed were the same ones used for RPLC analysis. In addition to the individual peak areas, a quantity labelled "degree of polymerization index" was also calculated. This is equal to the total area of peaks 1, 2, 3, and 4 (which correspond to products of higher molecular weight) divided by the sum of the areas of peaks 5 and 6 (which correspond mainly to the monomers DDS, TGDDM, and DGEBA).

Peak 1 corresponds to compounds of higher molecular weight. The exclusion limit for the column used is about 3500. Fig. 9(a) shows that there is little change in the relative area before 30 days exposure, at which point there is a sharp increase. There is a peak at this position in the chromatogram of the Novolac resin believed to be present in Narmco 5208. During the first 30 days, this epoxy species probably decreases due to reaction with amine, but at the same time new molecules of the same size are formed by reaction of smaller molecules. As a result, the overall size of this peak changes little until the Novolac species is consumed, at which point an increase is observed. It is interesting to note that the change in slope in Fig. 9(a) occurs around the same time that a significant change is observed in the curves obtained for the TGDDM-DDS reaction product by RPLC or HS-RPLC.

For the combined peaks 2 and 3, there is a steady increase in relative area, attributed to the expected formation of higher-molecular-weight components. However, there is a substantial degree of scatter, which is reflected in the relatively low squared correlation coefficient of 0.78 for the linear regression. Peak 4 remains fairly constant, no doubt for the same reasons as peak 1.

Peaks 5 and 6 are related mainly to the monomers DDS and TGDDM respectively (5). The DDS variation is shown in Fig. 9(b). As in RPLC, the DDS shows the most significant change, with a rate of decrease of 0.85% per day, which is slightly lower than the 1.05% found by RPLC. However, in RPLC the peak is well resolved and its intensity can be directly related to the amount of DDS present through the use of an internal standard. In HPSEC, the DDS peak involves contributions from other compounds which may not decrease with the aging; hence, the rate of decrease of the relative area is lower than in RPLC. The TGDDM also decreases steadily, and linear regression gives a line corresponding to a decrease of 0.39% per day, compared to 0.38% as measured by RPLC.

The "degree of polymerization index" is plotted in Fig. 10. There is a gradual linear increase over the first 40 days, followed by a more rapid increase beyond this point. This is about the same time at which the reaction product formed from TGDDM and DDS reaches its maximum level. It is the point at which the proportion of high-molecular-weight compounds (bigger than the TGDDM-DDS reaction product) becomes important.

Crabtree and Hewitt (8,23) have monitored the aging of Narmco 5208 at 22°C by size-exclusion chromatography and obtained chromatograms which resemble those reported here, except that the elution times were three times as long. The results were expressed quantitatively in terms of the ratios of certain pairs of peaks, and substantial changes (in the form of linear increases) were observed over a fifteen-day period. It is impossible to make a direct comparison with the results given here because ultraviolet detection was used rather than refractive index detection.

HPSEC is not as sensitive as RPLC for detecting variations among different batches, but it can be useful for following variations in the degree of advancement. The "degree of polymerization index" seems adequate for monitoring the sudden increase of high-molecular-weight species, but the peak of the hardener (DDS) is better for measuring the aging of the epoxy system.

Pyrolysis - capillary gas chromatography

A typical pyrogram of the Narmco 5208 prepreg is shown in Fig. 11. Quantitative results were obtained by taking the ratio of the areas of selected peaks in the chromatogram with respect to that of peak 2, the most intense peak, which corresponds to aniline.

Fig. 12 shows how the ratios vary with prepreg exposure time. In all cases, up to about 45 days there is no significant effect. Beyond this, a slight increase is observed. The fact that all the peaks show similar behaviour suggests that the real reason may be a decrease in the amount of aniline after 45 days. Generally speaking, this method is of little value for following the prepreg aging. This is not surprising, since aging simply changes the degree of polymerization of the resin, and pyrolysis results in "depolymerization". A better identification of all the major peaks could result in the finding of peaks which are specifically characteristic of higher-molecular-weight species. At the present time, the technique is of greater value for detecting variations in chemical composition, such as a change in the hardener/epoxy ratio (7).

Thermal analysis

Selected samples of aged prepreg were analyzed by differential scanning calorimetry. After the DSC measurement, the exact weight of resin in the specimen used was determined by a thermogravimetric method. The results are summarized in Table 4.

The second column gives the weight loss which occurs during the DSC measurement. As reported earlier (6), most of this occurs at higher temperatures. Up to 273°C, which is the upper limit for the integration of the DSC exotherm peak, the weight loss is less than 1% when nitrogen is used as atmosphere. Thus the measured value of ΔH is not significantly affected. However, in order to obtain a complete curve, the experiment is continued up to 320°C, and since above 300°C the weight loss is not negligible, it must be combined with the TGA results in determining the total resin content. This is given in the third column. It is seen that it varies significantly from

specimen to specimen. The values range from 38.6% to 46.6%, even though all specimens came from the same batch of prepreg.

To obtain meaningful values of the heat of polymerization, the area under the DSC peak must be divided by the weight of resin to give ΔH in joules per gram of resin. The fourth column of the table gives "uncorrected" values of ΔH, obtained by assuming that the resin weight is equal to 42% of the prepreg sample weight. This figure corresponds to the nominal resin content of the prepreg. While it can be seen that there is a gradual decrease with aging time, there is a large degree of scatter which would make it very difficult to accurately estimate the extent of aging by this method. The last column of the table gives the "corrected" ΔH values obtained by dividing by the true resin weight, as determined by TGA. In this latter case, the degree of scatter is much reduced. Linear regression gives a squared correlation coefficient of 0.91, as compared to 0.40 for the "uncorrected" case. The value of ΔH, which is directly related to the number of unreacted epoxy groups in the resin, decreases by 0.26% per day from its initial value of 561 J/g. This is somewhat lower than the figure of 0.34% obtained for the FT-IR epoxide index, which in theory is also related to the number of unreacted epoxy groups. One possible reason for the discrepancy is that two different epoxy resins are involved in the Narmco 5208 system, and the bisphenol A Novolac epoxy appears to react faster than the TGDDM-based one. If the two resins make different relative contributions to the IR epoxide index and the heat of polymerization, this may explain the difference between the results obtained by the two methods.

In spite of the reasonably good correlation obtained, DSC appears to be less sensitive than FT-IR or RPLC for detecting small changes in composition, such as those which occur in the first 20 days of aging. It also requires considerably more time, because of the thermogravimetric analysis needed to obtain reproducible ΔH values.

Samples aged under special conditions

The sheet of prepreg stored in a freezer at -25°C was tested after 87 days of storage and the results compared to those obtained at the beginning of the test period. No significant chemical changes were detected, confirming that freezer storage effectively inhibits the polymerization reaction.

The sheet of prepreg stored at room temperature under dry conditions was tested after 50 days, and in this case, significant changes were observed. Generally speaking, they were of about the same magnitude as those found in the prepreg exposed for 35 days at 50% R.H. Thus, in the absence of humidity, aging still occurs but at a somewhat lower rate.

CONCLUSIONS

Significant chemical changes occur at a steady rate when prepreg containing Narmco 5208 resin is exposed to the atmosphere at room temperature (22°C) and 50% relative humidity for a period of 66 days. These changes can be detected with varying degrees of sensitivity by several physicochemical techniques. The physical properties of the prepreg are also affected, and there is evidence that certain mechanical properties of cured panels prepared from the prepreg may be affected to some extent.

The best parameters for following the chemical changes which take place are the following:

- The "epoxide index" as determined by infrared spectroscopy, either in transmission or in attenuated total reflection. This is an indicator of the number of unreacted epoxide groups present; it decreases by 0.34% per day from its initial value under the conditions studied.
- The content of unreacted hardener DDS, as measured by reverse-phase high-performance liquid chromatography. It decreases by 1.05% per day. It can also be monitored (with somewhat poorer precision) by high-performance size-exclusion chromatography.
- The content of TGDDM-DDS reaction product, or the RP/TGDDM ratio, as measured by RPLC.

These parameters are only suitable in the initial stages of aging, because after a certain time (30 days in the present case), they stop increasing.

The following parameters are also affected by the aging, but are less suitable than those just described because of greater experimental error in their determination:

- The heat of polymerization ΔH of the resin, as determined by differential scanning calorimetry. It decreases by 0.26% per day. In order to obtain reproducible values of ΔH, the resin content of each specimen of prepreg analyzed must be determined by thermogravimetric analysis.
- The content of TGDDM monomer, as measured by RPLC. This decreases by 0.38% per day.
- The content of DGEBA monomer, as measured by RPLC. This decreases by 0.87% per day.
- The "degree of polymerization index", as determined by high-performance size-exclusion chromatography. This shows a gradual increase up to about 40 days, then a more rapid increase beyond this point.
- Certain other peaks found in the RPLC and HPSEC chromatograms.
- The ratios of certain peaks found in the pyrolysis – gas chromatogram. Significant changes are observed only after 40 days exposure time, so this method is not really of much practical use.

Narmco 5208 prepreg exposed to room temperature under dry conditions ages at a somewhat slower rate than prepreg exposed at 50% R.H. However, prepreg stored in a freezer at -25°C for 87 days showed no detectable change.

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Table 1. Results of linear regression analysis for various measured parameters. Figures given in parentheses correspond to calculated standard errors.

Technique	Parameter	Intercept		Slope		Squared correlation coefficient	Change per day
FT-IR Transmission	Multiple epoxide index	0.4068	(0.0013)	-0.001367	(0.000051)	0.981	- 0.34 %
	Single epoxide index	0.13537	(0.00044)	-0.000459	(0.000017)	0.980	- 0.34 %
FT-IR ATR	Multiple epoxide index	0.679	(0.012)	-0.00245	(0.00031)	0.969	- 0.36 %
	Single epoxide index	0.2352	(0.0024)	-0.000759	(0.000060)	0.988	- 0.32 %
RPLC	DDS peak area	4.036	(0.039)	-0.0424	(0.0018)	0.973	- 1.05 %
	DDS/TGDDM ratio	0.3164	(0.0019)	-0.002674	(0.000057)	0.984	- 0.85 %
	TGDDM peak area	12.95	(0.13)	-0.0493	(0.0040)	0.806	- 0.38 %
	DGEBA peak area	1.569	(0.019)	-0.01369	(0.00057)	0.941	- 0.87 %
	DGEBA/TGDDM ratio	0.1225	(0.0012)	-0.000766	(0.000037)	0.923	- 0.63 %
HS-RPLC	DDS peak area	4.97	(0.12)	-0.0539	(0.0034)	0.989	- 1.09 %
	DDS/TGDDM ratio	0.3281	(0.0058)	-0.00289	(0.00016)	0.991	- 0.88 %
	TGDDM peak area	15.59	(0.49)	-0.073	(0.013)	0.906	- 0.47 %
	DGEBA peak area	1.909	(0.054)	-0.0115	(0.0015)	0.952	- 0.60 %
	DGEBA/TGDDM ratio	0.12341	(0.00098)	-0.000251	(0.000027)	0.967	- 0.20 %
HPSEC	DDS peak relative area	25.94	(0.33)	-0.221	(0.010)	0.934	- 0.85 %
	TGDDM peak relative area	44.18	(0.79)	-0.174	(0.024)	0.596	-0.39%
DSC/TGA	ΔH	560.6	(4.4)	-1.45	(0.11)	0.911	- 0.26 %

Table 2. RPLC results (based on peak areas) for major peaks.

Prepreg Exposure Time (days)	Normalized peak areas with respect to acetophenone internal standard				Peak area ratios with respect to TGDDM peak		
	Peak 1 (DDS)	Peak 7 (RP)	Peak 9 (TGDDM)	Peak 10 (DGEBA)	Peak 1 (DDS)	Peak 7 (RP)	Peak 10 (DGEBA)
0	3.993	1.426	12.77	1.583	0.3128	0.1117	0.1239
2	3.988	1.504	12.59	1.473	0.3047	0.1149	0.1126
4	3.787	1.589	12.82	1.459	0.2953	0.1239	0.1138
7	3.716	1.600	12.81	1.485	0.2901	0.1249	0.1159
9	3.568	1.557	12.06	1.397	0.2988	0.1304	0.1171
11	3.457	1.584	11.96	1.367	0.2890	0.1324	0.1142
14	3.595	1.786	12.52	1.454	0.2872	0.1427	0.1162
17	3.365	1.759	12.41	1.349	0.2711	0.1417	0.1087
21	3.388	2.000	12.66	1.394	0.2677	0.1580	0.1101
25	3.159	2.039	12.37	1.320	0.2554	0.1648	0.1067
29	2.962	2.062	11.99	1.254	0.2471	0.1720	0.1046
32	2.741	1.996	11.55	1.134	0.2373	0.1729	0.0981
35	2.345	1.780	10.51	1.071	0.2231	0.1694	0.1019
38	2.250	1.772	10.22	0.965	0.2202	0.1734	0.0944
42	2.057	1.871	10.59	0.935	0.1942	0.1766	0.0882
45	2.023	1.864	10.71	0.929	0.1889	0.1741	0.0868
52	1.805	1.825	10.30	0.829	0.1754	0.1773	0.0804
59	1.638	1.820	10.30	0.801	0.1591	0.1767	0.0776
66	1.335	1.859	9.77	0.655	0.1366	0.1899	0.0670

Table 3. High-speed RPLC results (based on peak areas) for major peaks.

Prepreg Exposure Time (days)	Normalized peak areas with respect to acetophenone internal standard				Peak area ratios with respect to TGDDM peak		
	Peak 1 (DDS)	Peak 3 (RP)	Peak 4 (TGDDM)	Peak 5 (DGEBA)	Peak 1 (DDS)	Peak 3 (RP)	Peak 5 (DGEBA)
2	4.81	2.65	14.66	1.797	0.328	0.1804	0.1226
11	4.492	3.135	15.60	1.870	0.2880	0.2010	0.1199
25	3.689	3.202	14.04	1.648	0.2626	0.2279	0.1173
38	2.681	3.10	12.65	1.465	0.2119	0.2450	0.1158
66	1.494	2.69	10.69	1.131	0.1398	0.2521	0.1058

Table 4. Thermal analysis results.

Prepreg Exposure Time (days)	DSC wt. loss (%)	% Resin by wt.	ΔH (uncorrected) (J/g)	ΔH (corrected) (J/g)
0	2.2	44.6	581	548
0	1.2	40.0	525	552
0	2.7	42.8	555	545
7	4.1	41.5	540	546
7	4.1	43.6	577	556
17	3.6	40.3	507	529
17	0.0	39.3	526	562
17	3.1	39.2	515	552
17	3.6	39.2	513	549
32	4.4	45.0	554	516
32	2.7	38.6	478	520
42	3.0	45.1	530	494
42	2.6	42.4	506	501
59	4.5	46.6	512	462
59	4.4	46.1	511	465
66	3.6	43.9	494	472
66	0.4	45.5	498	460
66	3.8	45.0	504	470

CAPTIONS FOR FIGURES

Fig. 1. Chemical structures of Narmco 5208 components.

Fig. 2. FT-IR transmission spectrum of Narmco 5208 resin.

Fig. 3. Variation of (a) multiple and (b) single epoxide indices (as measured by IR transmission) as a function of prepreg exposure time. Unfilled symbols were not included in regression analysis.

Fig. 4. Variation of (a) multiple and (b) single sulfone indices (as measured by IR transmission) as a function of prepreg exposure time.

Fig. 5. Attenuated total reflection FT-IR spectra of Narmco 5208/WC3000 prepreg: (a) as received; (b) exposed 66 days at 22°C and 50% R.H.

Fig. 6. RPLC chromatogram of Narmco 5208 prepreg (THF extract).

Fig. 7. Variation of RPLC peak 7 (TGDDM-DDS reaction product) as a function of prepreg exposure time: (a) peak area normalized with respect to acetophenone internal standard; (b) peak area ratio with respect to TGDDM.

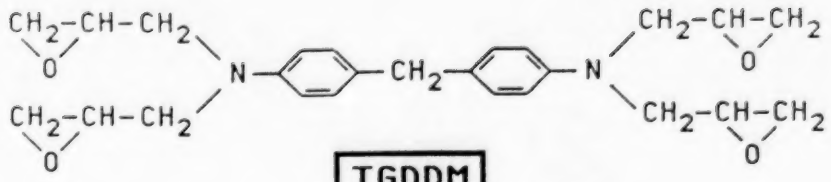
Fig. 8. HPSEC chromatogram of Narmco 5208 prepreg (THF extract).

Fig. 9. Variation of HPSEC peaks 1 (a) and 5 (b) as a function of prepreg exposure time.

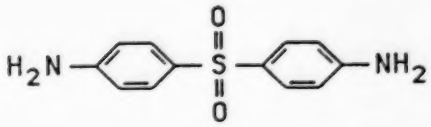
Fig. 10. Variation of "degree of polymerization index" (as measured by HPSEC) as a function of prepreg exposure time.

Fig. 11. Pyrolysis – capillary gas chromatogram of Narmco 5208 prepreg.

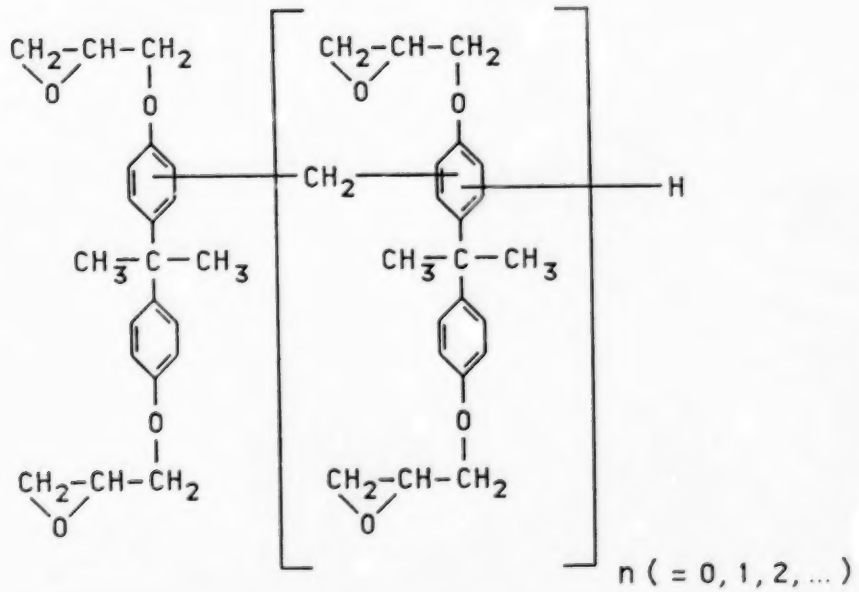
Fig. 12. Variation of peaks 3, 4, and 7 in the pyrolysis – gas chromatogram as a function of prepreg exposure time.



TGDDM



DDS



Bisphenol A Novolac Epoxy

Fig. 1

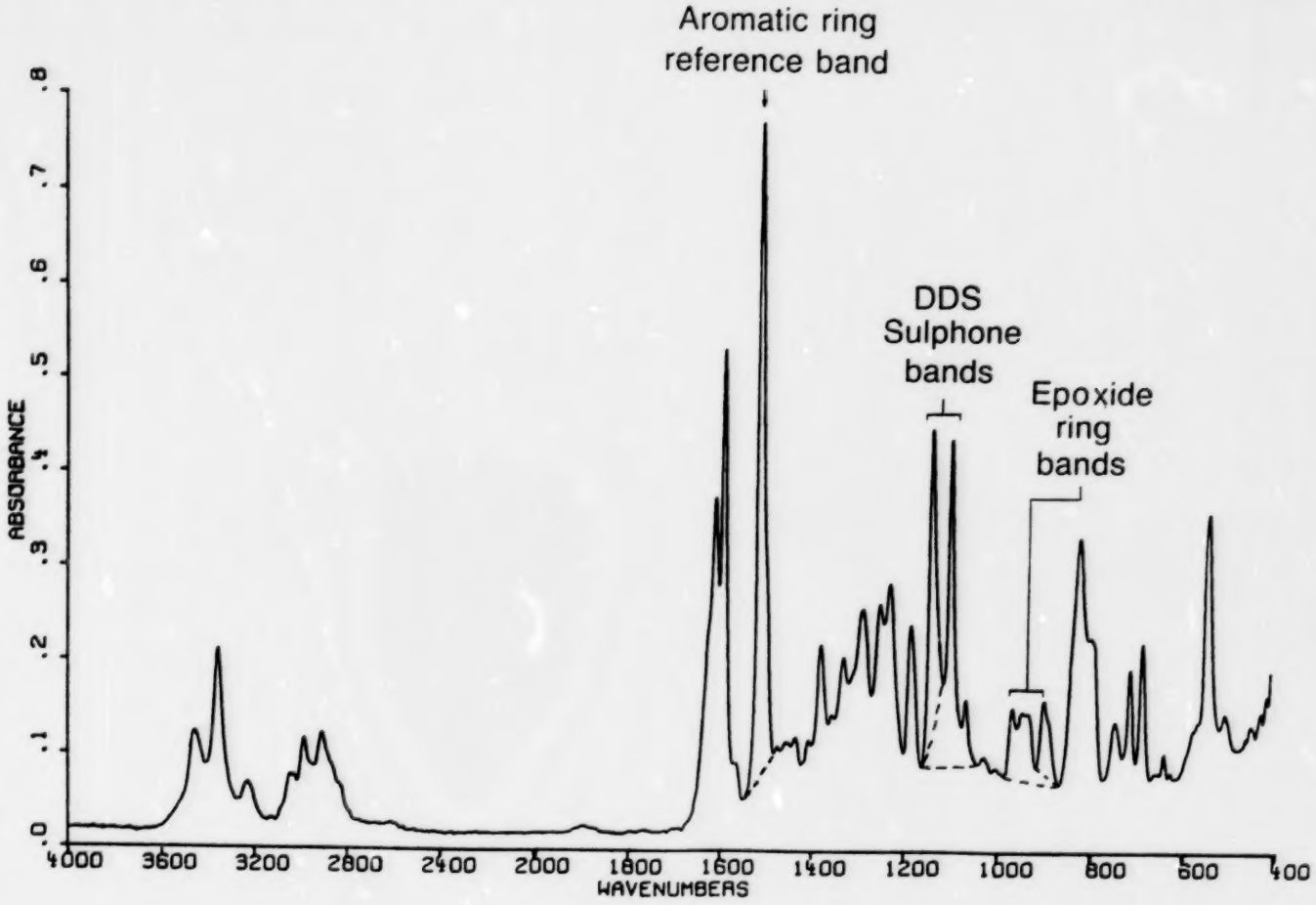

Aromatic ring
reference band
DDS
Sulphone
bands
Epoxide
ring
bands
ABSORBANCE
.0
.1
.2
.3
.4
.5
.6
.7
.8
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS

Fig. 2

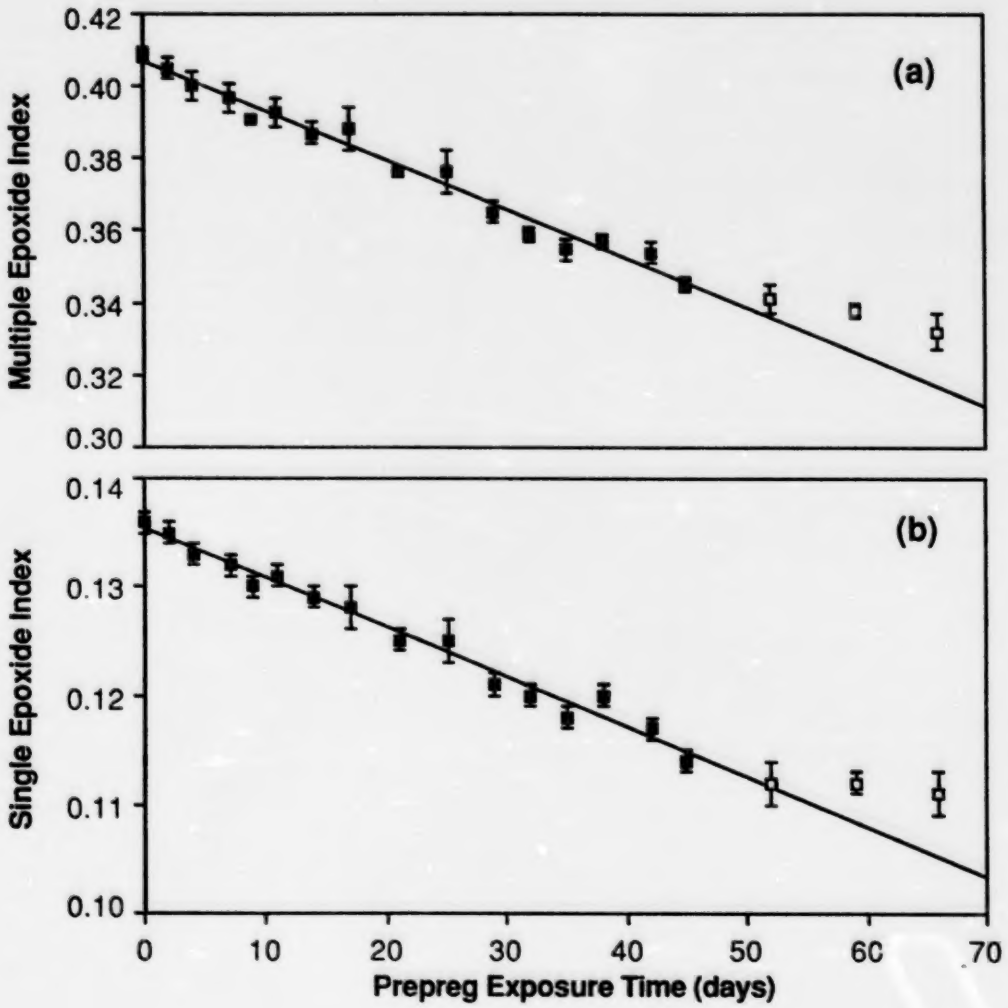

Multiple Epoxide Index
0.42
0.40
0.38
0.36
0.34
0.32
0.30
(a)
Single Epoxide Index
0.14
0.13
0.12
0.11
0.10
(b)
0
10
20
30
40
50
60
70
Prepreg Exposure Time (days)

Fig. 3

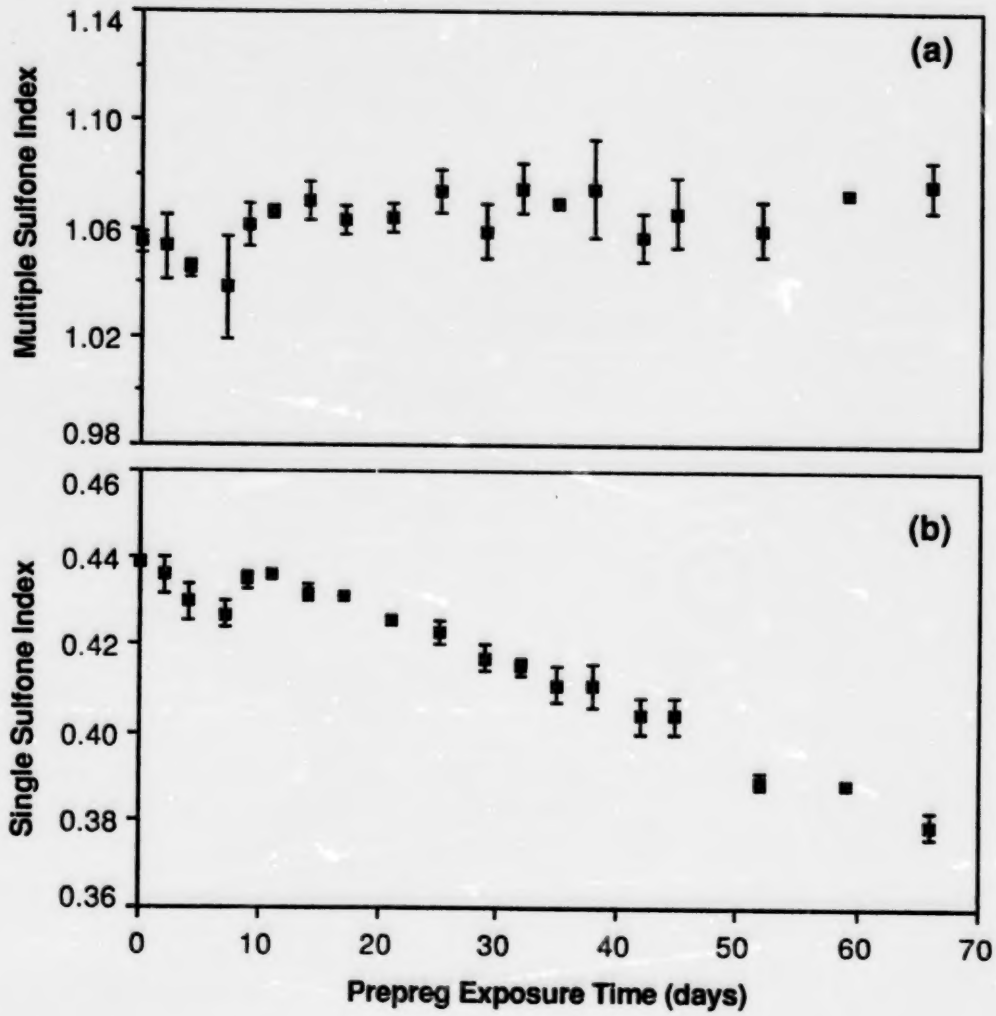

(a)
Multiple Sulfone Index
1.14
1.10
1.06
1.02
0.98
(b)
Single Sulfone Index
0.46
0.44
0.42
0.40
0.38
0.36
0
10
20
30
40
50
60
70
Prepreg Exposure Time (days)

Fig. 4

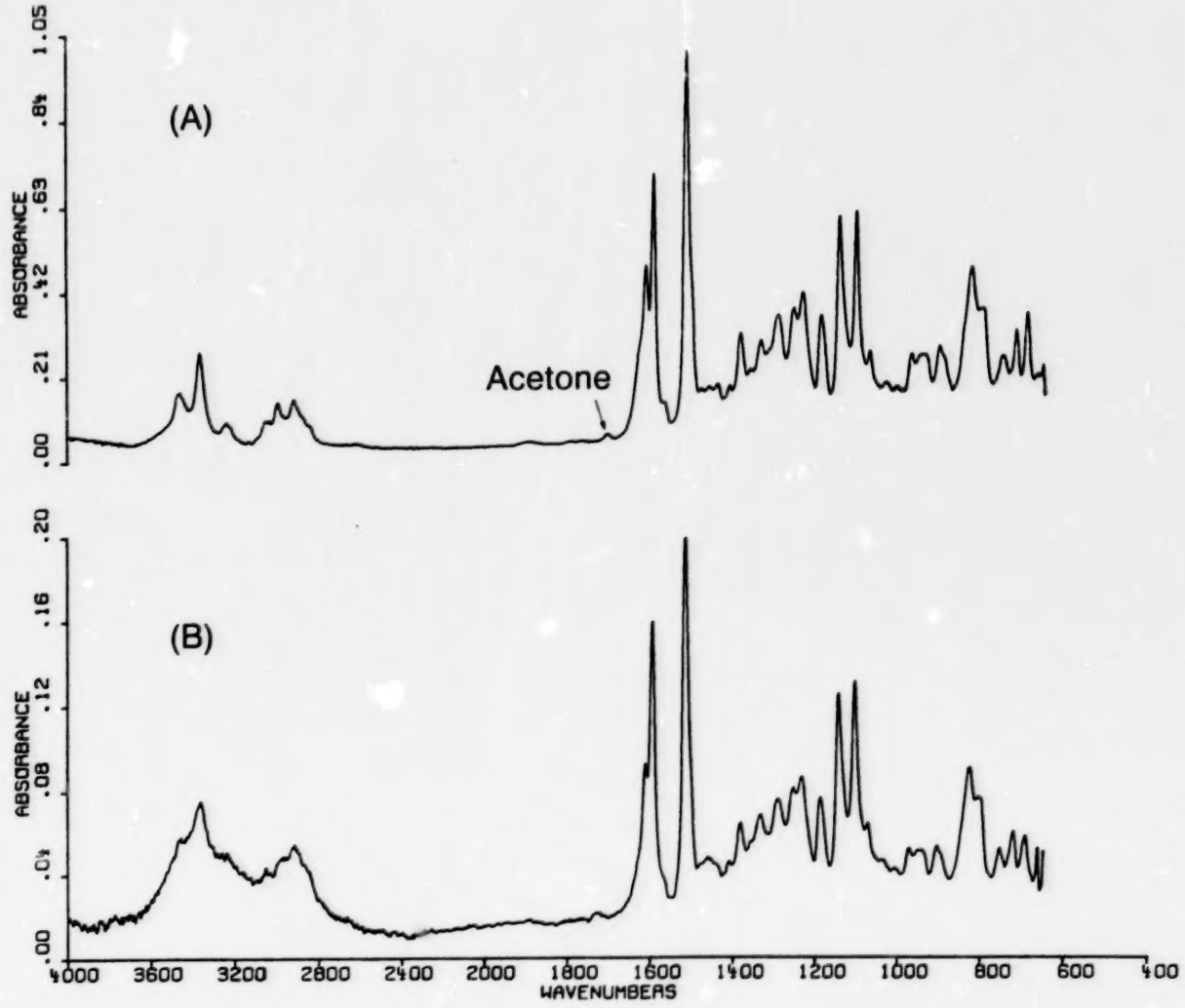

(A)
Acetone
ABSORBANCE
.00
.21
.42
.63
.84
1.05
(B)
ABSORBANCE
.00
.04
.08
.12
.16
.20
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBERS

Fig. 5

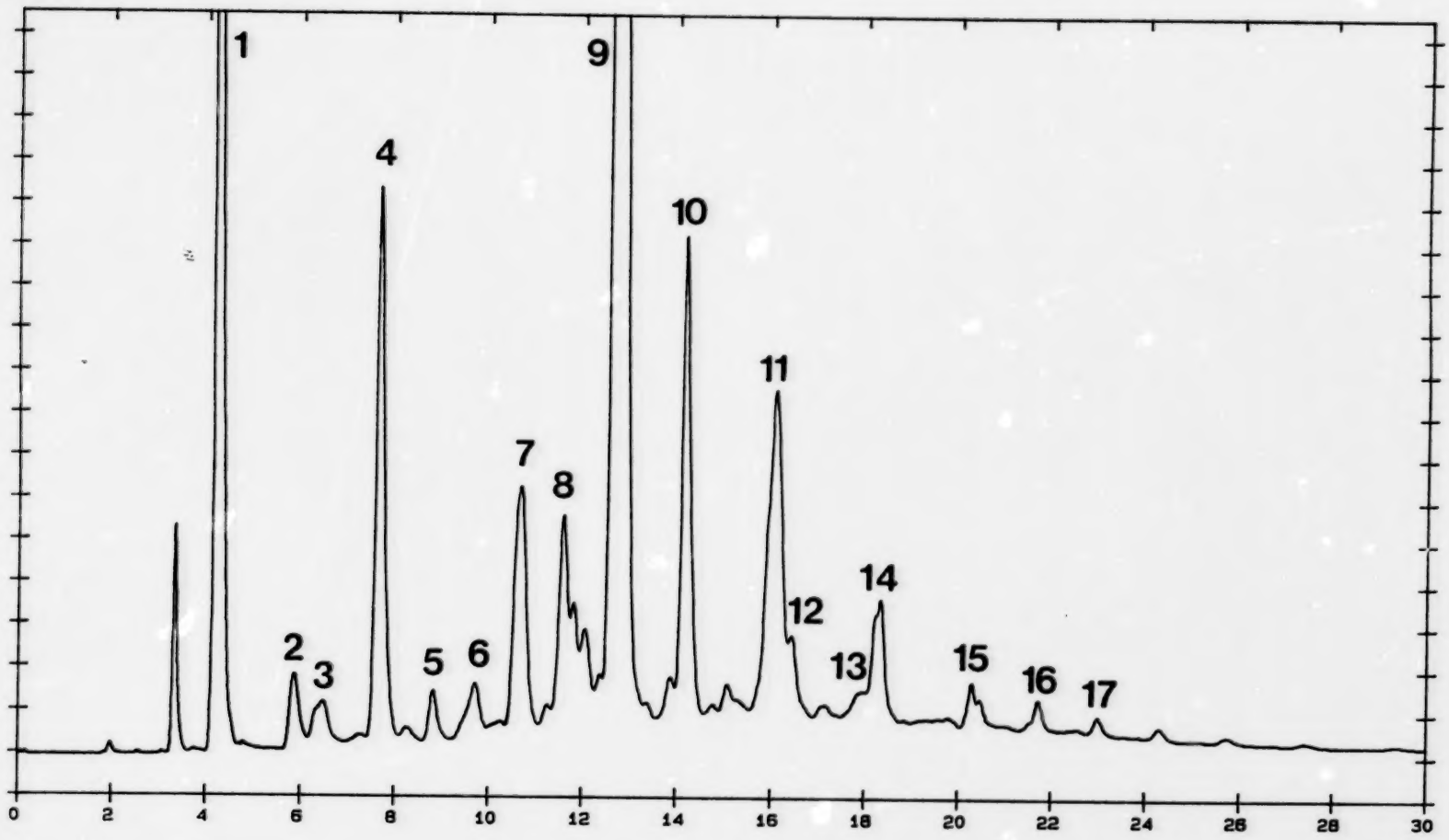

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
Retention time (min)

Fig. 6

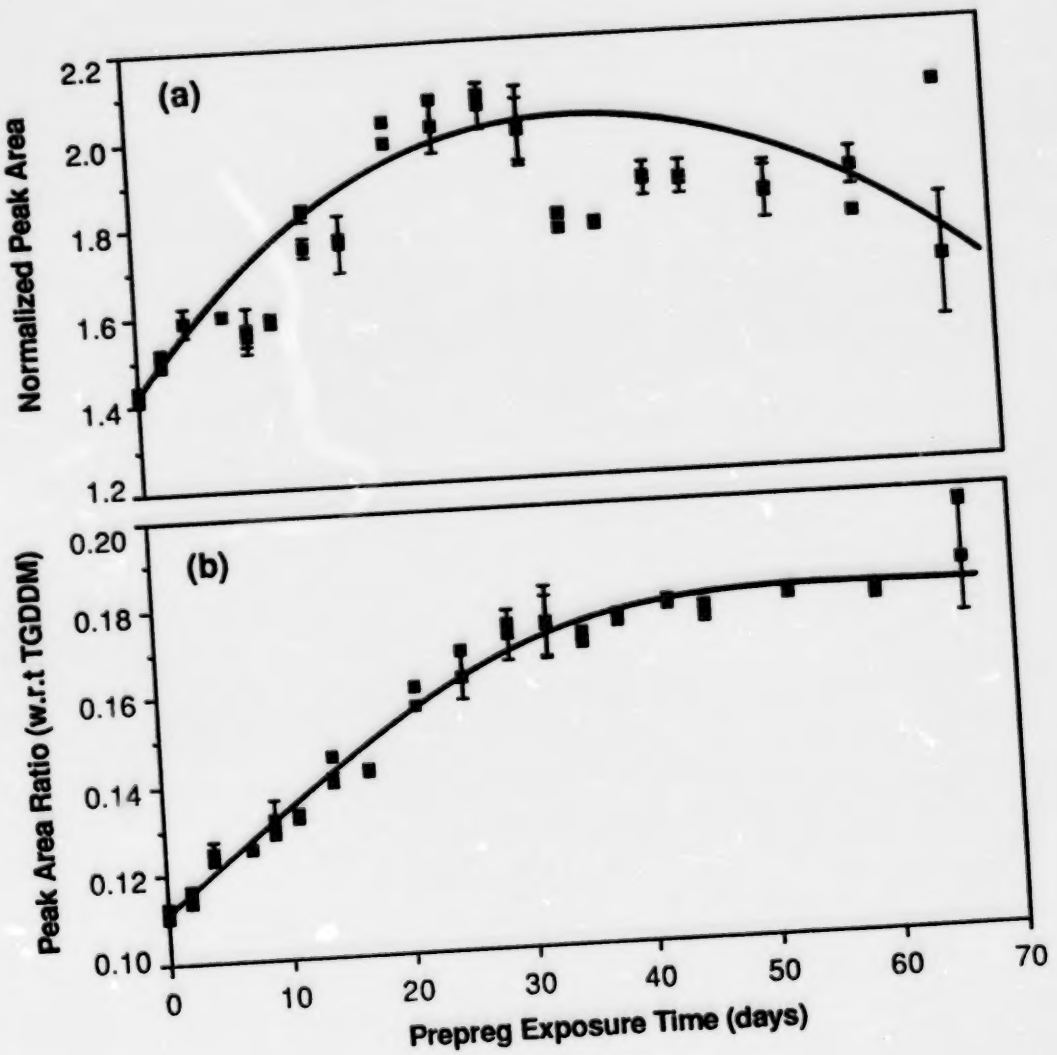

(a)
Normalized Peak Area
2.2
2.0
1.8
1.6
1.4
1.2
(b)
Peak Area Ratio (w.r.t TGDDM)
0.20
0.18
0.16
0.14
0.12
0.10
0
10
20
30
40
50
60
70
Prepreg Exposure Time (days)

Fig. 7

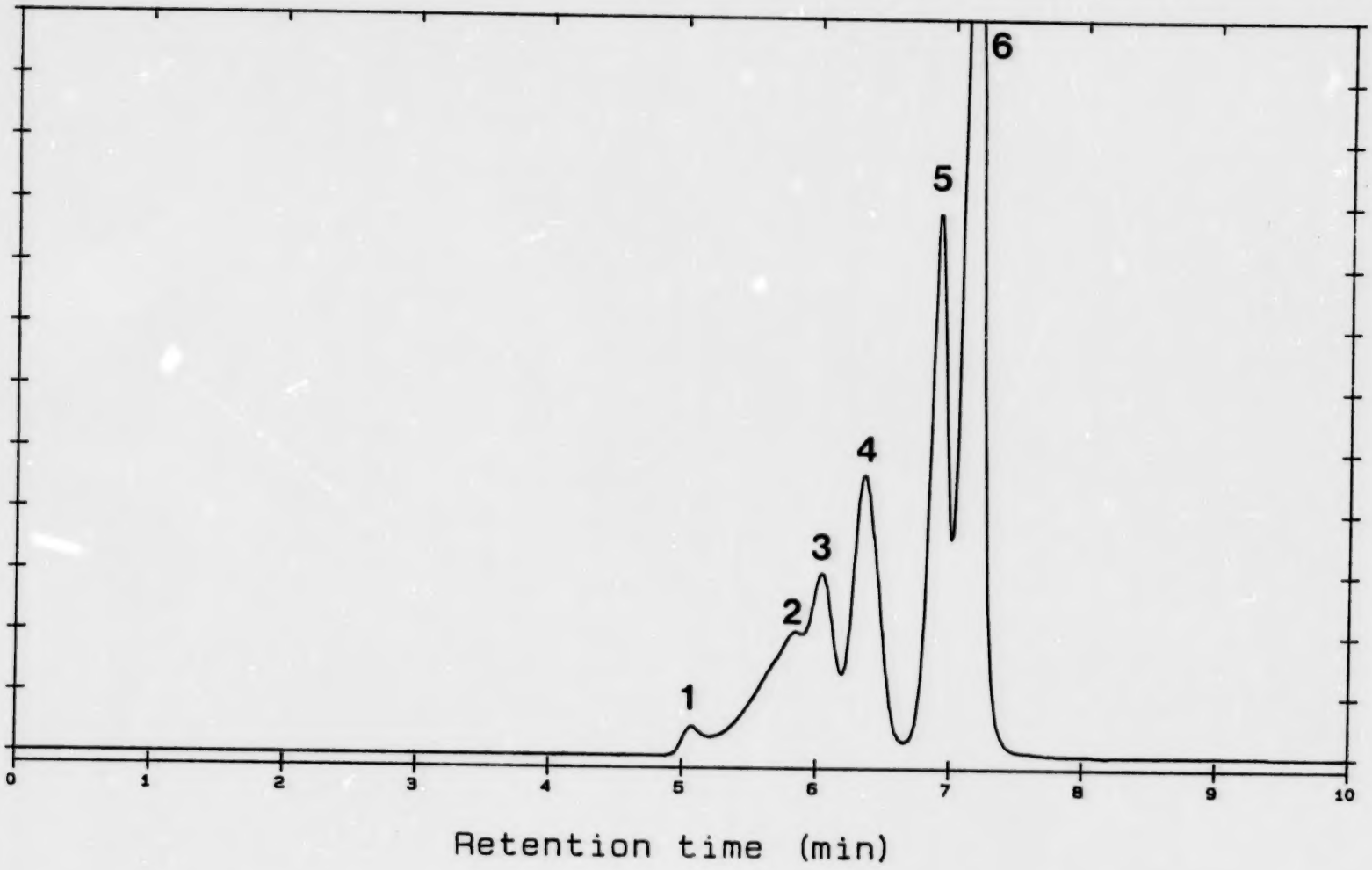


Fig. 8

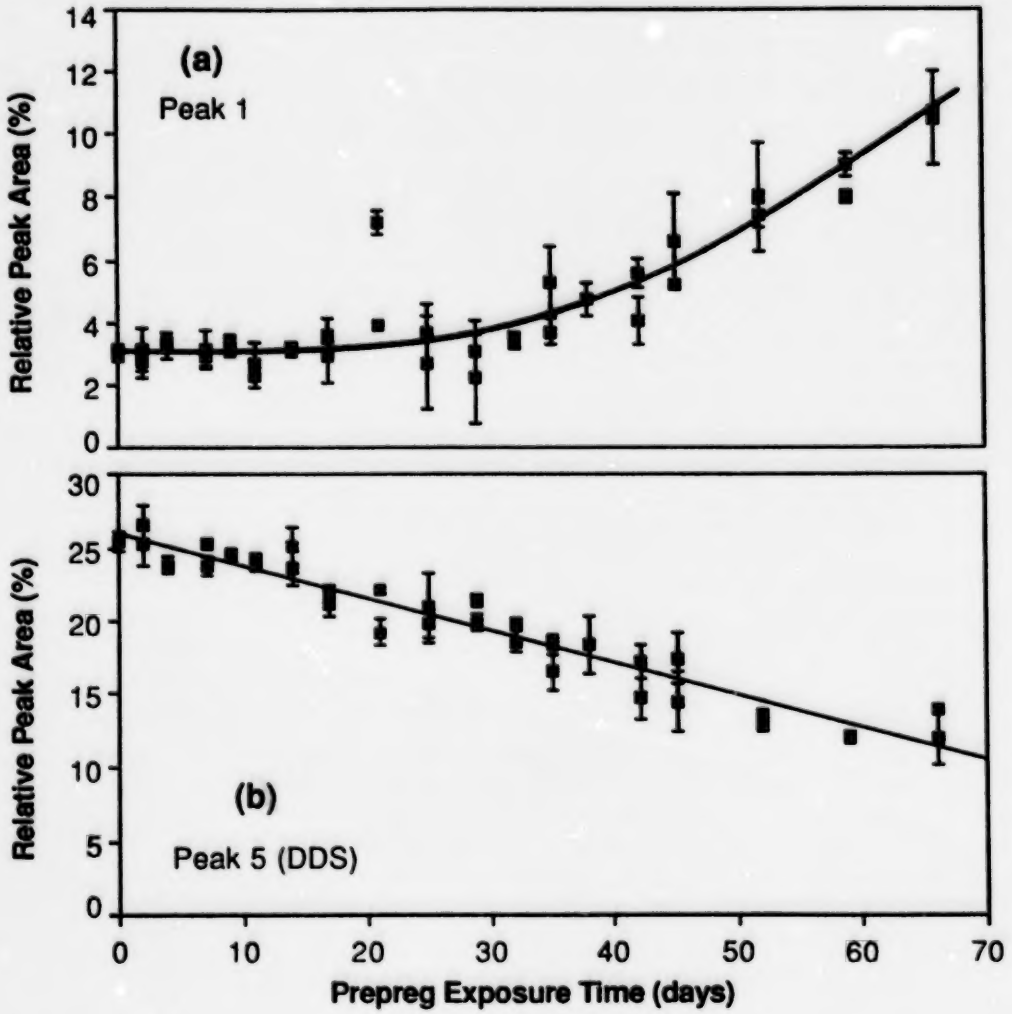

(a)
Peak 1
Relative Peak Area (%)
14
12
10
8
6
4
2
0
(b)
Peak 5 (DDS)
Relative Peak Area (%)
30
25
20
15
10
5
0
0
10
20
30
40
50
60
70
Prepreg Exposure Time (days)

Fig. 9

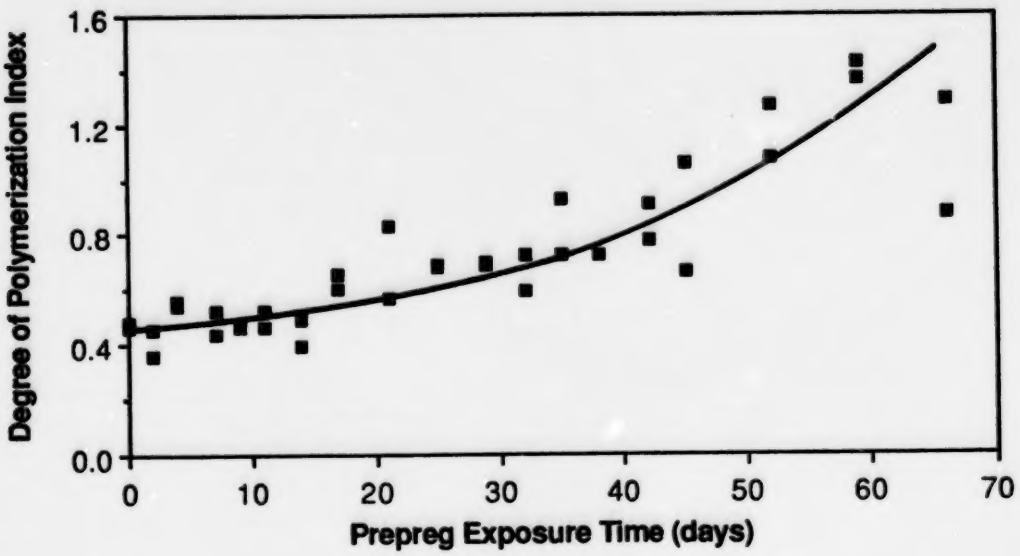
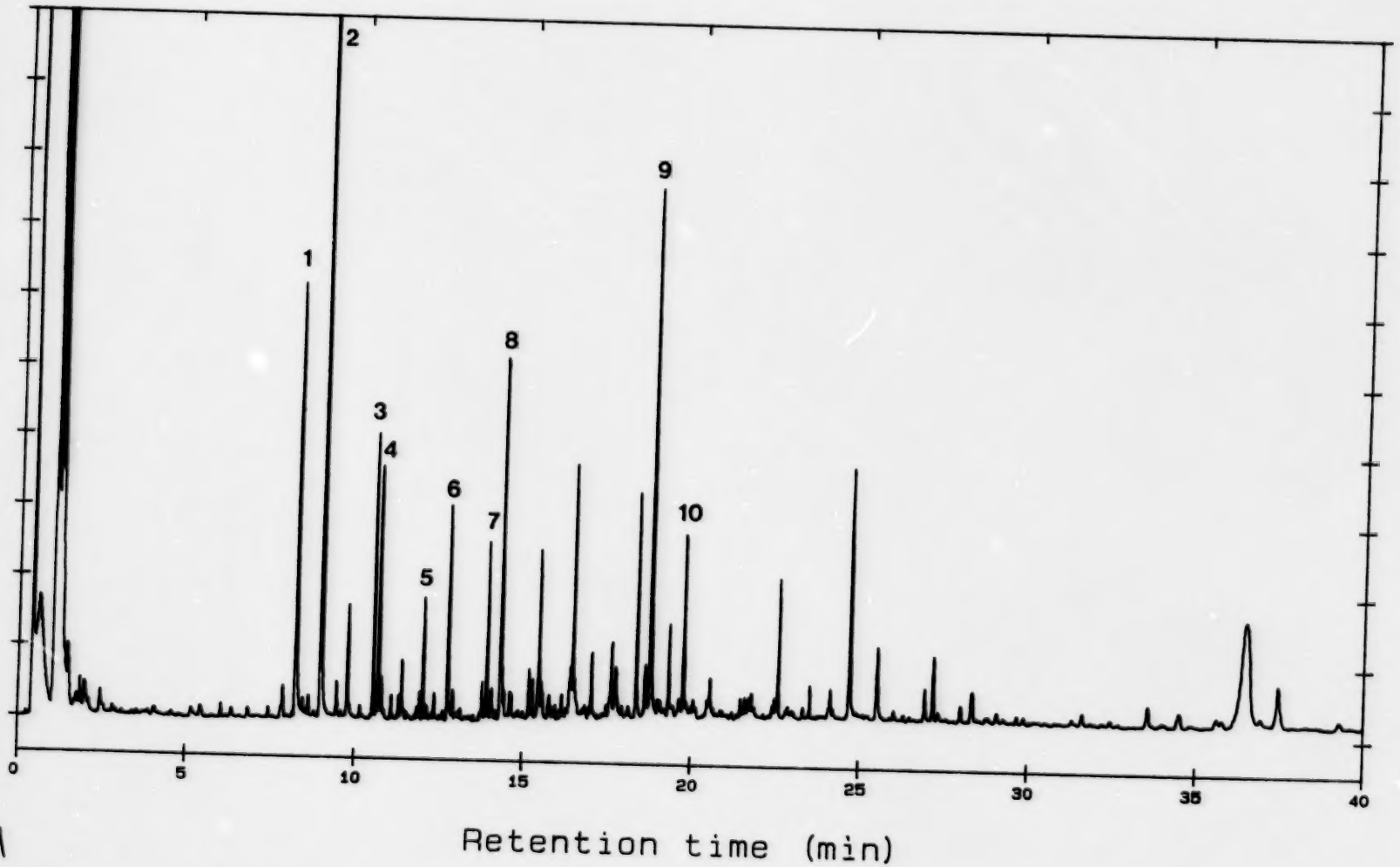

Degree of Polymerization Index
1.6
1.2
0.8
0.4
0.0
0
10
20
30
40
50
60
70
Prepreg Exposure Time (days)

Fig. 10


1
2
3
4
5
6
7
8
9
10
0
5
10
15
20
25
30
35
40
Retention time (min)

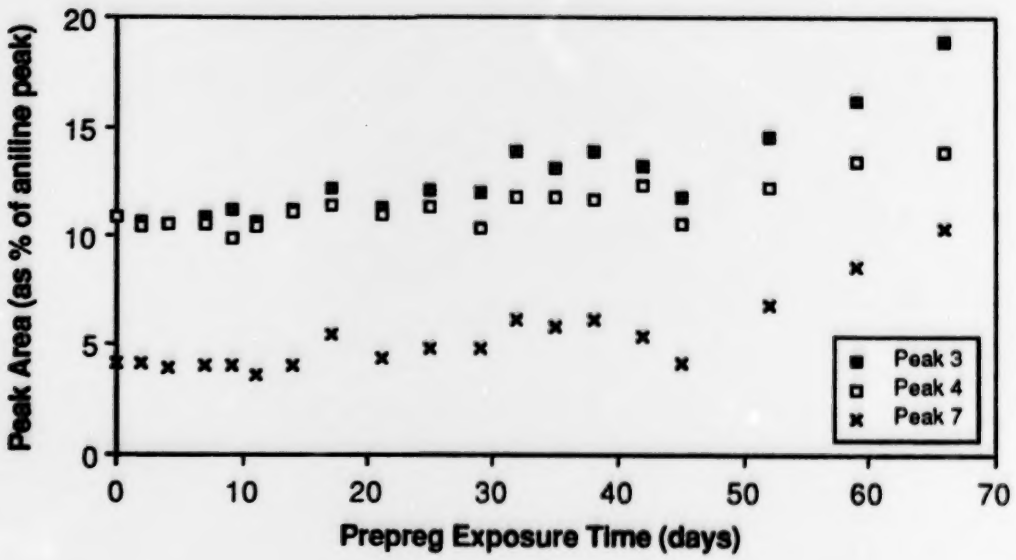

Peak Area (as % of aniline peak)
20
15
10
5
0
0
10
20
30
40
50
60
70
Prepreg Exposure Time (days)
Peak 3
Peak 4
Peak 7

Fig. 12